LLNL Environmental Restoration Division Standard Operating Procedure	TITLE: Field Measurements on Surface and Ground Waters
APPROVAL Date _____ _____ Environmental Chemistry and Biology Group Leader	PREPARERS: T. Carlsen, P. Daley, R. Goodrich, S. Gregory, and G. Howard REVIEWERS: R. Brown*, E. Christofferson*, V. Dibley, B. Failor*, J. Greci, B. Hoppes*, S. Kawaguchi. and B. Ward*
APPROVAL Date _____ _____ Division Leader CONCURRENCE Date _____ _____ QA Implementation Coordinator	PROCEDURE NUMBER: ERD SOP-2.2 REVISION: 2 EFFECTIVE DATE: December 1, 1995 Page 1 of 9

*Operations and Regulatory Affairs Division

1.0 PURPOSE

The purpose of this procedure is to ensure that water chemistry measurements on surface and ground water (i.e., pH, temperature, specific conductance, dissolved oxygen, redox potential, alkalinity and water level measurement) are properly performed and documented. These water chemistry measurements are performed in the field to determine stabilization of water chemistry within set parameters prior to sample collection. The measurements are also made to determine specific physical characteristics of surface water.

2.0 APPLICABILITY

This procedure is applicable when performing field collection and measurement of water quality parameters during ground water purging and at the time of sample collection.

3.0 REFERENCES

3.1 Korte, N. and P. Kearl (1984), "Procedures for the Collection and Preservation of Groundwater and Surface Water Samples and for the Instal Department of Energy," Grand Junction, Colo.

3.2 U.S. EPA (1979), *Methods for Chemical Analysis of Water and Wastes*, Washington, D.C. (EPA-600/4-79-020).

3.3 U.S. EPA (1992), *RCRA Ground-Water Monitoring: Draft Technical Guidance*, Washington, D.C. (EPA/530-R-93-001).

4.0 DEFINITIONS

4.1 Alkalinity ($CaCO_3$)

$CaCO_3$ is a measure of the quantity of mineral salts (i.e., carbonates, bicarbonates, hydroxides and occasionally the borates, silicates, and phosphates) that cause a sample to have a pH greater than 7. The alkalinity of the water is measured in milligrams per liter of $CaCO_3$ (mg/L).

4.2 Dissolved Oxygen (DO)

DO is the amount of oxygen dissolved in water at a given temperature. The dissolved oxygen content of a water sample at the time of collection is measured in milligrams per liter (mg/L).

4.3 Electrical Conductivity (EC) or Specific Conductance

EC is a measure of the ability of a material to conduct a current under the influence of an applied electric field. It is the reciprocal of resistivity and is measured in micro-mhos/cm (µmhos/cm).

4.4 Potential of Hydrogen (pH)

The hydrogen ion concentration of water is expressed as pH. The pH is measured on a scale from 0 to 14. It is a measure of the acidity or alkalinity of a solution, numerically equal to 7 for neutral solution. A pH less than 7 indicates an acid solution, whereas a pH greater than 7 indicates an alkaline solution. The pH is related to the hydrogen-ion concentration as follows:

$$pH = - \log [H^+]$$

4.5 Redox Potential (Eh)

Eh is a measure of a chemical reaction in which an atom or molecule loses electrons to another atom or molecule. The reaction is also known as oxidation-reduction. Oxidation is the loss of electrons, while reduction is the gain in electrons. The redox potential of water is measured in millivolts (mV).

5.0 RESPONSIBILITIES

5.1 Division Leader

The Division Leader's responsibility is to ensure that all activities performed by ERD at the Livermore Site and Site 300 are performed safely and comply with all pertinent regulations and procedures, and provide the necessary equipment and resources to accomplish the tasks described in this procedure.

5.2 Environmental Chemistry and Biology Group Leader (ECBGL)

The ECBGL is responsible for the approval of field instruments and any deviation from procedures, as well as ensuring field personnel are trained to properly perform tasks to the appropriate procedures. The ECBGL or appropriate task leader are responsible for providing field personnel information for non-routine sampling tasks.

5.3 Field Personnel

The field personnel's responsibility is to collect and measure water quality parameters during purge time and at sample collection time according to the guidelines herein.

5.4 Sample Coordinator (SC)

The SC's responsibilities are to 1) supply a quarterly Routine Ground Water Sampling Schedule, Well Specification Table, and/or a daily specific sample plan (Daily Operations Guide), and 2) check the incoming LLNL Ground Water Sampling Log for field measurements to ensure parameters are stable prior to collection of ground water samples.

5.4 Task Leader/Group Leader

A task leader or group leader's responsibilities are to provide information to the SC and field personnel for non-routine sampling tasks.

6.0 PROCEDURE

There are several advantages in taking measurements of water chemistry in the field vs. taking measurements in the laboratory. A major advantage is the ability to immediately resample and reanalyze on site if a particular sample is suspected to be unrepresentative or not valid. Another advantage is that field measurements of water chemistry (pH, specific conductance, temperature, and alkalinity) may differ from laboratory measurements due to changes in the amount and types of dissolved constituents (mainly gases). The disadvantages of obtaining field measurements usually relate to the reliability and sensitivity of the particular method and equipment used for the test.

6.1 Office Preparation

6.1.1 Prior to commencement of field activities, personnel shall review the appropriate Site Safety Plan and all associated SOPs and OSPs. Current copies of all relevant documents shall be retained in the sample vehicle at all times.

6.1.2 The quarterly Routine Sampling Schedule is provided by the SC to the field personnel for routine ground water sampling. The schedule declares the number and identification of wells for which field chemistry measurements need to be obtained, as well as other purging and sampling information.

6.1.3 The sampling schedule for treatment facilities appears in waste discharge permits. The schedule declares the location and frequency for field chemistry measurements that need to be taken. A task or group leader will provide this information for non-routine sampling points. Logbook entries of sampling activities and field measurements are to be made in the appropriate treatment facility logbook.

6.1.4 Coordinate schedules/actions with the SC or with the ECBGL or appropriate task leader.

6.1.5 Obtain the Water Sampling Logbook from the SC. Assemble a sufficient number of field forms to complete the field assignment. Instructions for completing the logbook entries and field forms are provided in SOP 4.2, "Sample Control and Documentation." An example sample entry is located inside the cover of the Water Sampling Logbook.

6.1.6 The sampling personnel are responsible for maintaining the field instrumentation used to measure water quality parameters according to the manufacturer's instructions. The sampling contractor orders or ensures the availability of the standard solutions for electrical conductivity and pH calibrations. Calibration standards should be changed before the standard expiration dates. The SC or QC Chemist may periodically check solutions to verify that the standards can be traced using the National Institute of Standards and Technology (NIST) and are within shelf life.

6.2 Field Preparation

6.2.1 Assemble the appropriate water sampling equipment and field chemistry instrumentation according to Attachment A. Check to ensure that equipment and instruments are properly working.

6.2.2 Calibrate or verify the calibration of field chemistry instrumentation according to SOP 4.8, "Calibration/Verification and Maintenance of Field Instruments Used in Measuring Parameters of Surface and Ground Water and Soils."

6.3 Operation

6.3.1 Record all preliminary information (i.e., document control numbers, well ID, casing depth, casing diameter, etc.) on the Ground Water Sampling Log.

6.3.2 The following data fields should be filled in on the LLNL Ground Water Sampling Data Sheet and/or in the appropriate field logbook when collecting water chemistry measurements using the following instruments:

A. Specific Conductance Meter ID. Identification, model, or serial number of specific conductivity meter being used.

B. pH Meter ID. Identification, model, or serial number of pH meter being used.

C. Flow Cell ID. Identification, model, or serial number of flow cell being used for acquisition of temperature, specific conductance and pH.

D. Water-Level Indicator ID. Identification, model, or serial number of water level indicator used.

E. Calibration Information. Record calibration information for the pH and specific conductance meters in the water sampling field logbook prior to purging and sampling ground water.

6.3.2. Measure the depth to water and record water level on the LLNL Ground Water Sampling Log.

6.3.3 Take an initial set of field water chemistry measurements from the first available water from the well (Sections 6.3.5) and record field constituents (e.g., pH, temperature and specific conductance) on the LLNL Ground Water Sampling Log. Field personnel are to complete all lines on the form. If some steps are not taken or not applicable (NA), indicate that in the appropriate space. Complete the forms with nonwater-soluble ink (not felt-tip) pens. Any variation in these procedures must be explained on the form.

6.3.4 Subsequent water chemistry measurements should be taken after each well casing volume purged. A final set of measurements should be obtained as close to the time of sampling as possible. When sampling wells under RCRA (Resource Conservation and Recovery Act) guidelines, an additional set of field measurements should be taken at 2-minute to 3-minute intervals at the end of the third well casing volume and prior to sample collection (SOP 2.1, "Presample Purging of Wells," and SOP 2.7, "Presample Purging and Sampling of Low Yielding Monitor Wells").

6.3.5 pH Measurements

A. The meter should have a temperature probe and be capable of temperature compensation.

B. Meters should be calibrated according to the owner's manual at the beginning of each day and recorded in the assigned field logbook (see SOP 4.8.

C. Collect the sample in a clean container (e.g., a glass beaker) that has been rinsed with the liquid to be sampled. In some sampling events, a flow-through cell can be used to obtain measurements. This limits the effects of the exposure to air.

D. Using a squeeze bottle filled with deionized water, thoroughly rinse probe, and pat dry with a clean tissue. Rubbing the probe may cause a static discharge that will disrupt measurements.

E. Place the probe into sample. Obtain readings according to the instrument's operating manual. Record readings on the LLNL Ground Water Sampling Log.

F. Remove probe and again, thoroughly rinse with deionized water and pat dry. Depending on probe type, return to buffer solution or dry storage.

NOTE:

After calibration, the pH probe should be kept in a beaker of water or buffer solution, if necessary. Some field pH probes are specially constructed and do not require continuous submersion. Be sure to check the owner's manual.

6.3.6 Temperature

Temperature readings are usually obtained from the temperature probe used to compensate the pH measurements and can be read directly off the pH meter. A separate temperature probe may be used and should read to the 0.1°.

6.3.7 Electrical Conductivity (EC)

A. As with pH meters, EC meters should also be capable of temperature compensation.

B. Meters should be calibrated just prior to the first sampling event of the day, according to the owner's manual (SOP 4.8).

C. Clean probe and cable with deionized water and clean tissues. Conductivity probes are commonly hollow, therefore it is also necessary to squirt deionized water through probe.

D. Measure conductivity in a clean container that has been rinsed with the liquid to be sampled or using a flow-through cell. Record conductivity periodically throughout the time of purging, according to the schedule specified in SOP 2.1, "Presample Purging of Wells." Record the position of each setting on the meter. Choose a scale appropriate for the specific conductance of the sample.

E. Rinse the probe in distilled water and dry it completely before returning it to the calibration solution.

F. Most conductivity probes produce an electrical field that may be disturbed if the probe is near a solid object. Therefore, keep the probe at least 2 in. away from the cell walls or bucket.

6.3.8 Dissolved oxygen and redox potential

Meters that measure dissolved oxygen and redox potential are more specialized instruments, and are operated under the supervision of the ECBGL or designee. The ECBG or designee chooses the instrument and ensures that it is properly calibrated and operated.

6.3.9 Alkalinity ($CaCO_3$)

Determination of sample alkalinity at the time of sampling is generally done using an alkalinity kit. Like dissolved oxygen and redox potential, the procedure is somewhat more specialized. The ECBGL or designee chooses the appropriate kit and ensures that personnel are trained to use it.

6.4 Post Field Operation

6.4.1 Clean and/or decontaminate equipment as noted in the SOP 4.5, "General Equipment Decontamination."

6.4.2 Check that all field measurement data are recorded on the LLNL Ground Water Sampling Log (SOP 2.1, Attachment A).

6.4.3 Collect ground water samples when field measurements show stability. Stability is established when 1) there are no upward or downward trends apparent, 2) pH is within 0.1 pH unit, 3) temperature is within 0.5°C, and 4) specific conductance is within 50 µmhos/cm.

6.6 Office Post Operation

6.6.1 Inventory sampling equipment and supplies. Repair or replace all expendable, broken or damaged equipment.

6.6.2 Return equipment to proper storage area or SC, and report incidents of malfunctions or damage.

6.6.3 Deliver original forms and logbooks to the SC.

6.6.4 The SC will retain a copy of the original forms (CoC, ground water sampling log), and provide the originals to the Data Management Group (DMG) for final archive. The DMG will provide copies of the forms to the appropriate Operations and Regulatory Affairs Division Analyst, as necessary.

7.0 QA RECORDS

7.1 Chain-of-Custody forms

7.2 Logbooks

7.3 LLNL Ground Water Sampling Log

8.0 ATTACHMENTS

Attachment A—Equipment checklist

Attachment A

Equipment Checklist

The purpose of the list presented below is to aid field personnel in identifying those supplies necessary to conduct a particular field operation. It is not intended to be all inclusive. It is the responsibility of field personnel to determine and obtain the supplies required for successful performance of assigned tasks.

Attachment A. Equipment checklist.

Reagents	Yes	No	Comments
Alkalinity kit			
Check reagent volumes			
Check glass for breakage	_____	_____	
pH meter(s)	**Instrument 1**	**Instrument 2**	**Comments**
Check electrode			
Full of fluid			
Glass intact	_____	_____	
Check by immersing in tap water			
Check and calibrate it			
Rinse and fill			
Replace cap	_____	_____	
E_C meter			**Comments**
Check battery	OK _____	dead _____	
Check in tap water	OK _____	faulty _____	
Check against:			
Calibration solution	_____	_____	
Solution temperature	_____	_____	
Conductivity of solution	_____	_____	
Hand-held thermometer	**Yes**	**No**	**Comments**
Temperature			
Ice water	_____	_____	
vs laboratory thermometer			